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A New Silarylene-Siloxane Monomeric Resin for Structural Composites: Cure-Chemistry Insight and Thermal Properties of the Cured Matrix

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FOREWORD

Reported here are the synthesis and characterization of a siloxane-silarylene liquid monomer, which is a promising new resin component for the fabrication of tough carbon-fiber-composite parts that survive stowage in hot-wet environments and surface temperatures at high-Mach flight speeds.

The report describes the results of research conducted at the Naval Air Warfare Center Weapons Division (NAWCWD), China Lake, California, from October 2011 through September 2012.

This report was reviewed for technical accuracy by Dr. Stephen Fallis, Chemistry Division, NAWCWD, China Lake, California. This effort was supported by the NAWCWD 219 program. Additional funding was provided by the Office of Naval Research Code 35 Sea-Based Aviation Structures and Materials program.

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14. ABSTRACT

(U) Reported here are the synthesis and characterization of a siloxane-silarylene liquid monomer, which is a promising new resin component for the fabrication of tough carbon-fiber-composite parts that survive stowage in hot-wet environments and surface temperatures at high-Mach flight speeds. A model compound for the type of reactive end groups used was cured and analyzed by chromatography and mass spectrometry to give insight on the crosslinking and chain-extending structures that form during the curing process.

15. SUBJECT TERMS

2PEPPSi2, Cured Matrix, Disiloxane-silphenylene, Monomeric Resin, PEP, Phenylethynylenephenylene, Silarylene, Siloxane,

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ACRONYMS

µL	microliter
2PEPPSi2	1-3-bis(4-phenylethynylphenyl)-1,3-diphenyl-1,3-dimethyldisiloxane; PEP-terminated 1,2-diphenyl-1,2-dimethyldisiloxane
abs	absolute
ATR	attenuated total reflectance
$CDCl_3$	deuterated chloroform *or* deuterochloroform
cm	cubic meter
DIP-MS	direct insertion probe–mass spectrometry
DSC	differential scanning calorimetry
EtOAc	ethyl acetate, ethyl ethanoate
FTIR	Fourier transform infrared spectroscopy
GC/MS	gas chromatograph/mass spectrometer *or* gas chromatography/mass spectrometry
M	molar
MHz	megahertz
min	minute
mL	milliliter
mmol	millimole
mTorr	millitorr
NAVAIR	Naval Air Systems Command
NMR	nuclear magnetic resonance (*spectroscopy*)
NWC	Naval Weapons Center
$PdCl_2$	palladium(II) chloride
PEP	phenylethynylenephenylene
ppm	part per million
Tg	glass transition temperature
TGA	thermogravimetric analysis
T_m	melting temperature

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INTRODUCTION AND SUMMARY

Reported here is the preparation of a new monomer for resin formulations for binding carbon fibers. The monomer has promising properties for use in structural composites for Naval Air Systems Command platforms that are stowed in hot-wet environments and that must survive high-Mach aeroheating. This siloxane-silarylene monomer was discovered to be a liquid having low volatility that thermally cures to a tough, high-modulus solid. The cured material was stable to 450°C in air. The structure of this monomer is 1,2-diphenyl-1,2-dimethyldisiloxane terminated with phenylethynylenephenylene (PEP) end groups (in the *para*-configuration). A model compound for the PEP end groups was cured and analyzed by chromatography and mass spectrometry to give insight on the crosslinking and chain-extending structures that form during the curing process. Additional data were obtained on the volatility of the liquid monomer, on the increase in glass transition temperature (Tg) of the solid, and on the decomposition of the cured material as functions of time and temperature.

NAVY'S NEEDS

Current commercial resins are inadequate for making the structural-composite parts needed for future Navy platforms that must survive stowage in hot-wet environments and supersonic/hypersonic aerodynamic heating. Such a resin needs to be more easily processed in liquid form. Environmentally, it must be safe to manufacture and have no toxic off-gas. The liquid resin must wet the carbon fiber during resin-transfer molding and the manufacture of towpreg for filament winding yet must remain nonvolatile during the entire fiber-infusion process and curing operation. The resin must offer several days of storage life before the prepreg is cured at elevated temperatures. In addition to ultralow moisture uptake, better impact resistance and toughness are needed to survive rough shipboard handling and in-flight cyclic loading. The raw materials for the new resin and the process for making and curing the prepreg must be affordable.

TECHNICAL BACKGROUND

Over 60 years of published work by other investigators on silaryl-siloxane polymers provides an excellent launch pad for the present work (for example, see References 1 through 10). Important early Department of Defense work on these materials was performed in the 1980s by Robert Rhein (References 6 through 9) at the Naval Weapons Center (NWC) (now the Naval Air Warfare Center Weapons Division) (China Lake,

California) (sponsored by the Office of Naval Research). The disiloxane-silphenylene building block was chosen for the new resin of the present study because of its excellent thermal stability and hydrophobicity. As a result of using a large percentage of silarylene in the resin, an aromatic-carbon char will begin to form on the surface of the part at about 900°F (during aerodynamic heating). As a bonus, the siloxane component offers a degree of oxidation resistance because it forms a protective silica coating on the surface of the char when heated in the range of 1,000 to 1,100°F. This overlying silica layer retards further oxidation of the underlying char. A silica barrier coating also forms when the part is exposed to atomic oxygen in low-earth orbit (see References 11 and 12 and references therein).

Some of the earliest related work was performed by Lenz et al. (References 13 and 14) at the University of Massachusetts. They reported thermal degradation properties for a series of silarylene-siloxane high polymers (Reference 14). The linear high polymers that had no crosslinking groups underwent backbiting and unzipping of the chain ends at temperatures over 350°C (660°F). However, when a small percentage of the methyl side groups on the silicon atoms were replaced with vinyl groups for crosslinking and when a *p,p*-diphenyl ether segment was included in the backbone, the onset of degradation was increased to 410°C (770°F). Even higher performance can be achieved by placing certain reactive groups on the chain ends.

Forty years ago, Landis et al. at Hughes Aircraft pioneered ethynyl end groups for crosslinking high-temperature resins (Reference 15). A decade later, Harris et al. showed that phenylethynyl end groups gave a better combination of a larger thermal-processing window and greater thermo-oxidative stability (Reference 16).

In an article published 15 years ago (Reference 17), Bucco and Keller described a monomer closely related to the one reported here that was based on tetramethyldisiloxane with PEP end groups (compound 7b in Reference 14). However, 7b was far too volatile near the thermal curing temperature (>290°C), losing 50% of its mass before curing. Bucco and Keller also explored the carborane unit that improved oxidation resistance, but carborane is very expensive and was not included in the present study.

The analogous tetraphenyldisiloxane PEP monomer was reported (as a model compound) in a 2010 paper from China (Reference 18). However, that model compound melted sharply at 210°C (410°F) and therefore is not a good candidate resin for low-temperature or solvent-free liquid processing.

A useful discovery, reported in the results and discussion section, was that placing vicinal methyl and vicinal phenyl side groups on the same disiloxane unit greatly lowered the volatility (to about 11%) and that the resin remained liquid at room temperature for months with only a few percent residual ethyl acetate. It soon became obvious, however, that a monomer with higher molar mass was necessary to eliminate volatility of the monomer at the temperature required to cure PEP end groups (the onset of cure is about 300°C [570°F]). That work is in progress (star-shaped monomers).

TECHNICAL APPROACH

The overall goal of this study is to synthesize and characterize novel siloxane-silarylene-based aryl-ethynylene-terminated monomers and to assess their capabilities in resin formulations for fiber-infusion processing and, furthermore, to assess the capability of the cured resin to survive hot-wet hypersonic/supersonic flight conditions (using simulated time-temperature-humidity testing).

The definitions used in this report are as follows. A resin is a formulation of monomers and additives. A monomer is a relatively low-molar-mass liquid molecule comprised of a backbone and two or more reactive groups. The backbone may be linear, branched, or star shaped. The present study examines a linear monomer. The reactive groups are placed on the ends of the backbone, the ends of the branches, and the ends of the arms of the star.

The (phenylene-disiloxane-phenylene) building block was chosen for the present study because it enhances the following desirable properties: (1) low moisture uptake, (2) liquid processing without the use of solvents, (3) thermal stability, and (4) impact resistance. The flexible silicon-oxygen-silicon (disiloxane) segment imparts fluidity to the uncured resin and toughness to the cured resin. Siloxane segments longer than disiloxane can lead to degradation of the backbone above 350°C by a well-known ring-splitting mechanism (Reference 14). Crosslinking further improves the thermal stability and gives resistance to attack by environmental fluids.

As a guide for improving the end-group cure chemistry, one of the objectives of the present study was to identify the specific structures that build molecular weight and form crosslinks. A monomer having 1,2-dimethyl-1,2-diphenyldisiloxane mid segment and PEP end groups was chosen for this initial study (called 2PEPSi2). After a thorough search of the literature, a reference to this monomer was not found. The PEP reactive groups afford a long pot life (days) at a reasonable processing temperature (about 25 to 45°C). Furthermore, as described in the section entitled “Thermolysis of Tolane: A Model Reaction for Crosslinking Chemistry,” when cured above 320°C, PEP end groups form bulky, aromatic reinforcing junctions in the crosslinked matrix material.

A major objective of this study is to explore structures formed during uncatalyzed thermal curing in the temperature range of about 320 to about 390°C. Toward that end, the model compound diphenylacetylene (also called tolane) was thermalized at 350°C, and the reaction products were injected into a gas chromatograph–mass spectrometer

(GC/MS).[1] The results were quite enlightening and are described in the section entitled "Thermolysis of Tolane: A Model Reaction for Crosslinking Chemistry." Additional insight on the PEP curing process was obtained on 2PEPSi2 using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and TGA-Fourier transform infrared spectroscopy (TGA-FTIR).

There have been reports of diacetylene repeat units in siloxane-silarylene backbones, as well as incorporating isolated ethynylene repeat units in the backbone. However, when these polymers are cured at high temperatures, they typically become brittle solids ("brick dust"). Thus, unsaturation in the backbone is not part of the present study.

The two covalent backbone bonds by which phenylenes are attached to adjacent backbone segments can be in the *para*- and/or *meta*-configurations. The monomer reported here has *para*-configured PEP end groups. *Meta*-configurations will be explored next year, as they suppress crystallization.

EXPERIMENTAL PROCEDURES

MATERIALS

Ether, tetrahydrofuran, and an n-butyllithium solution were obtained from Aldrich and used as received. Bromo-4-iodobenzene and ethynylbenzene were obtained from TCI America and used as received. In addition, 1,3-dichloro-1,3-diphenyl-1,3-dimethyldisiloxane was obtained from Gelest Inc. and used as received. It contained a few percent of the trisiloxane and tetrsiloxane oligomers, as measured by GC/MS. The GC/MS analysis also showed the expected *d, l,* and *meso* diastereomers of the disiloxane unit.

ANALYTICAL EVALUATIONS

The nuclear magnetic resonance (NMR) spectra were obtained on a Brüker spectrometer (300 MHz). DSC thermograms were obtained on a TA Instruments Q100 V9.9 (build 303). TGA was performed using a TA Instruments Q5000 V3.10 (build 258). In a separate experiment using a TA Instruments TGA (Q50 V20.10, build 36) equipped with a heated gas cell and transfer line, the off-gases from a resin sample were analyzed in a Thermo Nicolet Nexuus 6700 FTIR spectrometer. The reported spectra are an average of 32 scans (baseline and background corrected).

[1] Note that GC is used interchangeably throughout this document to denote gas chromatograph and gas chromatography and that MS is used interchangeably for mass spectrometer and mass spectrometry.

The mass spectra of a liquid resin sample were analyzed by the direct insertion probe–mass spectrometry (DIP-MS) method using a ThermoFisher DSQII mass spectrometer.

To gain insight on the cure mechanism, the model compound diphenylacetylene (tolane) was thermalized, and the products were analyzed using GC/MS. An Agilent 6890 GC equipped with an Agilent 5973 MS detector was used. The GC used a Crossbond® Restek Rsi-5ms 20-meter column with a 0.18-mm-inside-diameter column packed with 5% diphenyl/95% dimethylpolysiloxane.

SYNTHESIS: A SCHEME FOR PREPARATION OF PRECURSOR TO PEP END GROUP

The scheme is to synthesize 1-bromo-4-(phenylethynyl)benzene; see Figure 1.

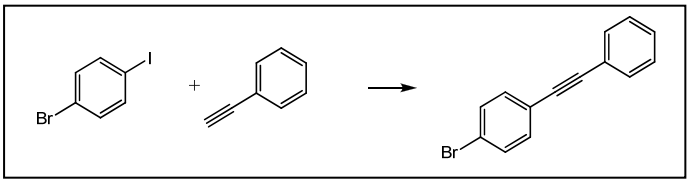


FIGURE 1. Chemical Structure of 1-Bromo-4-(phenylethynyl)benzene.

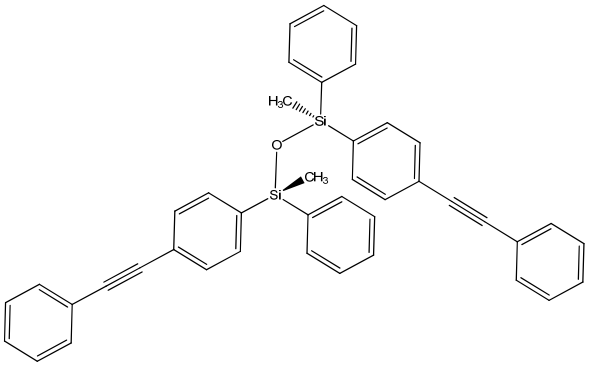
According to the procedure reported in Reference 19, the following quantities were added to a degassed mixture of 25 mL water and 8.3 mL pyrrolidine (100 mmoles): 0.04 gram $PdCl_2$ (0.2 mmole) and 5.66 grams 4-bromoiodobenzene (20 mmoles). The mixture was heated to 50°C, and 2.7 mL ethynylbenzene (24 mmoles) was added. The mixture was stirred at 50°C for 18 hours and then cooled. The solids were filtered off and washed with water to give 6.27 grams of a brown solid. This was chromatographed on silica gel using hexanes to give 2.60 grams of a white solid (51%). The results are as follows—^{1}H NMR ($CDCL_3$): multiplet centered around 7.5 ppm; ^{13}C NMR ($CDCl_3$): 133.16, 131.77, 131.44, 128.75, 128.60, 122.75, 122.30, 122.14, 90.30, 87.92.

The preparation of the 1-3-bis(4-phenylethynylphenyl)-1,3-diphenyl-1,3-dimethyldisiloxane (2PEPPSi2) was as follows. A solution of 2.35 grams 1-bromo-4-(phenylethynyl)benzene (9.1 mmoles) in 25 mL ether was cooled to 0°C while 3.7 mL 2.5-M n-butyllithium (9.2 mmoles) was added. The solution was stirred for 30 minutes at 0°C, and then a solution of 1.50 grams 1,3-dichloro-1,3-diphenyl-1,3-dimethylsiloxane (4.6 mmoles, 0.5 equivalent) in 10 mL ether was added dropwise. The mixture was allowed to warm to room temperature and then stirred for 18 hours. The solids were filtered off, and the filtrate was concentrated in vacuum to give 2.89 grams of a thick oil. This was chromatographed on silica gel using 10% EtOAc/hexanes to give 2.27 grams of a clear thick oil that solidified to a wax after several months (82% yield, which included 12% ethyl acetate). The results are as follows—^{1}H NMR ($CDCl_3$): 7.5 (m, 16H),

7.36 (m, 12H), 0.61 (s, 6H); ^{13}C NMR ($CDCl_3$): 137.85, 137.07, 134.00, 133.92, 131.68, 130.77, 129.81, 128.35, 127.87, 124.51, 123.26, 90.27, 89.46, -0.66; mass spectrum: 610 [M].

RESULTS AND DISCUSSION

The PEP-terminated 1,2-diphenyl-1,2-dimethyldisiloxane monomers are called 2PEPPSi2 (see the left side in Figure 2). Thus far, only the *para*-PEP isomer (*p,p*) has been synthesized. The *meta*-PEP isomer is also under construction because it should frustrate the tendency to crystallize. A mixture of isomers may further frustrate crystallization. The Tg of 2PEPPSi2 and this compound's tendency to crystallize are characterized in the section entitled "DSC Analysis."

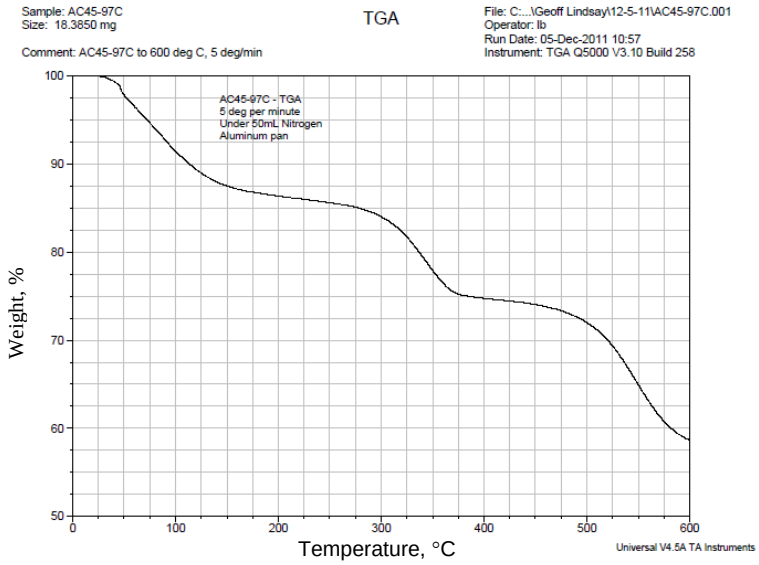


Note: The actual monomer was a mixture of diastereomers.

FIGURE 2. Chemical Structure of 2PEPPSi2 (*p,p* Isomer).

THERMOGRAVIMETRIC ANALYSIS

The initial 2PEPPSi2 oil recovered after chromatographic purification contained residual solvent. Figure 3 shows the TGA scan of this material heated at 5°C/min in a nitrogen atmosphere. The solvent (later identified as ethyl acetate) evaporated by the time the temperature reached 150°C. A plateau in weight loss occurred from 150 to 290°C. The mass loss (~11%, normalized to resin) between 290 and 380°C can be primarily attributed to volatilization of 2PEPPSi2 molecules, as determined by additional analytical measurements reported in the section entitled "TGA-TFIR Spectral Analysis." A final plateau in mass loss was observed between 380 and 460°C. Beyond 460°C, the mass loss is presumably due to the volatilization of chemical decomposition products formed during ceramification of the matrix. Extrapolation of the curve indicates there could be greater than 50% char remaining (absent oxygen).



Note: TGA in nitrogen, column-purified sample (13% residual ethyl acetate).

FIGURE 3. Thermogravimetric Scans at 5°C/min in Nitrogen.

Most of the solvent was removed from the liquid resin by pumping in vacuum at room temperature overnight. Figure 4 shows the TGA scan of this material heated at 5°C/min in air. The small amount of remaining solvent (~2%) came off prior to reaching 90°C. Another few percent weight loss occurred prior to reaching 290°C and was due to residual butyl-functional disiloxane-PEP resulting from the use of excess n-butyllithium in the synthesis of 2PEPPSi2 (more evidence is shown in the section entitled "DIP-MS on 2PEPPSI2"). In contrast to nitrogen, in air, a larger amount of weight loss was observed between 290 and 380°C (~17% in air, ~11% in nitrogen). In air some of the weight loss could possibly be oxidative degradation (e.g., volatile organoperoxides). In air, an abrupt onset of weight loss was observed at 550°C (1,025°F). This resin should naturally form a "self-healing" thermal-oxidative silica barrier coating on the outside skin of a platform at aerodynamic heating above 540°C (1,000°F). About 50% char remains at 600°C.

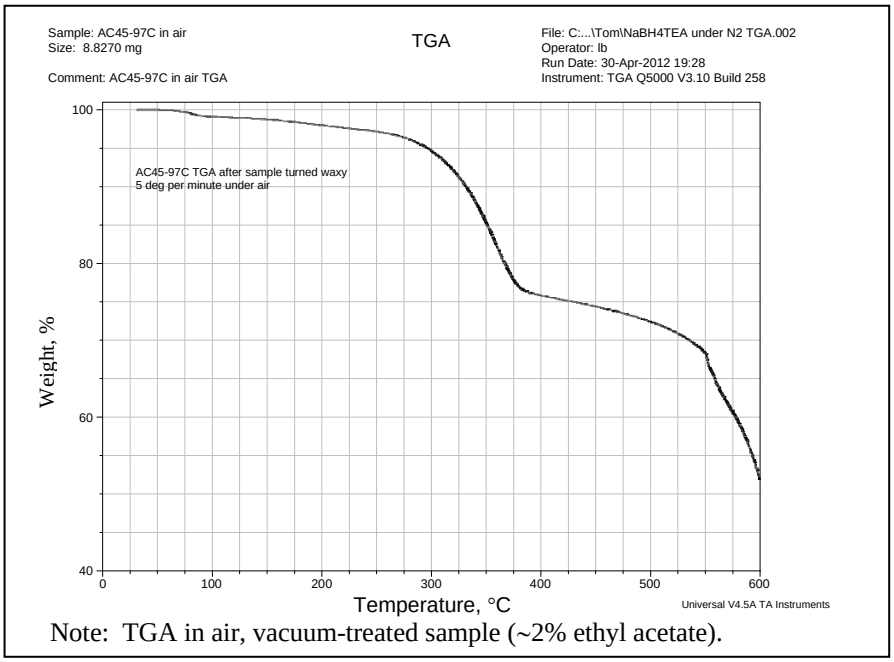
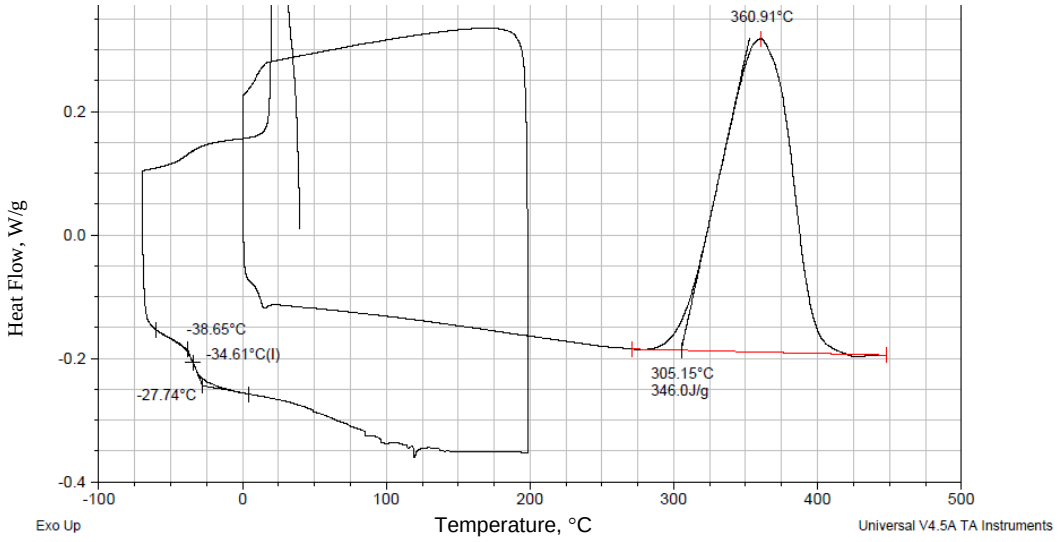


FIGURE 4. Thermogravimetric Scans at 5°C/min in Air.

DSC ANALYSIS

Figure 5 is a DSC thermogram (in nitrogen) of the original 2PEPPSi2 sample containing 12% ethyl acetate. Plasticization of the resin by solvent depressed the Tg of the starting resin to -34°C. In the second heating scan, the Tg increased to about +8°C, the result of evaporation of ethyl acetate in the first heating scan (note the broad endotherm from 30 to 130°C). The second heating scan clearly shows the crosslinking exotherm between 300 and 400°C. The evaporation of 2PEPPSi2 between 300 and 350°C would have appeared as an endotherm, but the large crosslinking exotherm completely masked the process. A second DSC analysis was performed on the vacuum-treated 2PEPPSi2, which had aged several months. This waxy resin had a broad melting endotherm (60 to 120°C) with a peak at 98°C (about the same melting point as the tetramethyl analogue [Reference 17]).

Since the exothermic curve returned to the baseline at 400°C (Figure 5) and remained constant to 450°C, it was concluded that the cured resin is stable to 450°C (840°F) in nitrogen (also in air, as shown by TGA, Figure 4). After this sample had cooled to ambient, a metallic tweezers tip was jammed into the cured sample, and the texture was observed to be very hard and tough. No cracking was observed.

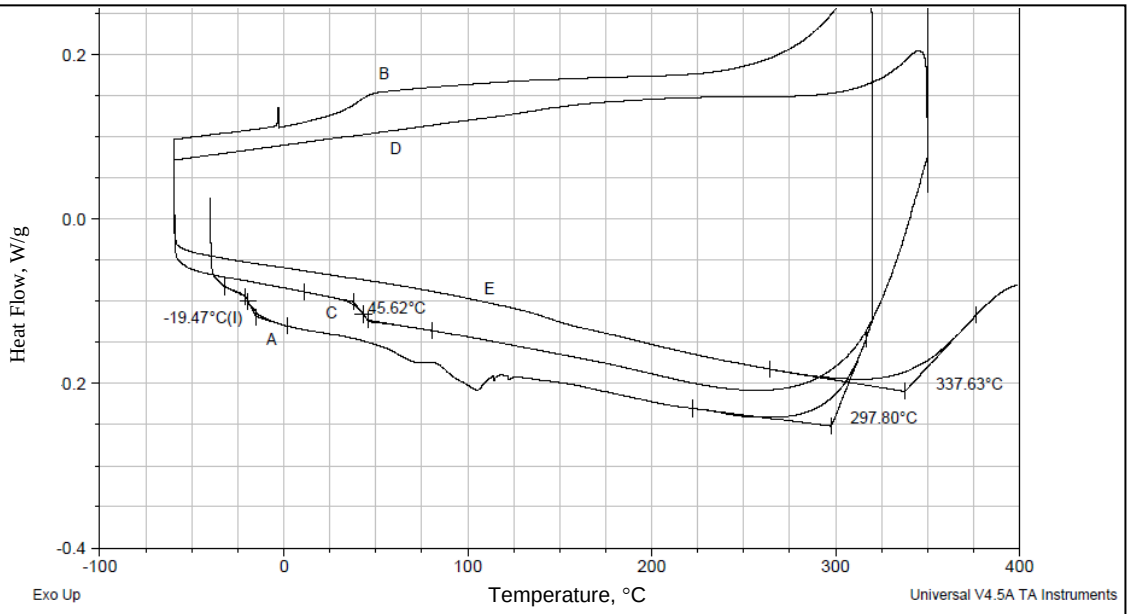


Note: The first heating rate was 10°C/min to 200°C; then the sample was immediately cooled to 0°C at 10°C/min. The final heating rate was 5°C/min.

FIGURE 5. DSC Thermogram in Nitrogen of Original 2PEPPSi2 Resin Plasticized With Residual Ethyl Acetate.

On the vacuum-treated sample, another DSC study in air was performed to measure the increase in Tg as a function of annealing time in the temperature region where uncatalyzed curing is thermally initiated. The DSC heating, annealing, and cooling protocol is shown in Figure 6. In the first heating scan (curve A), after the sample was equilibrated at -40°C, the Tg of the liquid resin was -19°C, in contrast to +8°C in the second heating scan of Figure 5, a result that confirms that a few percent of ethyl acetate remained in the vacuum-treated sample.

In Figure 6, curve A shows the onset of an exotherm at 270°C continuing throughout the 10-minute anneal at 320°C. Then the sample was cooled to -60°C. In the second heating scan (curve C), the Tg increased to 45°C. This higher Tg is also seen in the cooling-curve B and indicates that a solid with a higher molecular mass has formed. After the second heating ramp (curve C), the sample was annealed at 350°C for 20 minutes, at which the exotherm continued to increase. On the third heating scan (curve E), the slight change in heat capacity between 135 and 155°C is likely a broad Tg and is evidence for the conversion of the resin to a high-molecular weight (even crosslinked) solid during the 350°C anneal. In the third heating curve, the onset of the crosslinking exotherm was not observed until the temperature reached 320°C. As the temperature approached 400°C, the curing rate slowed down.



Note: Scan rate was 5°C/min. Curve A—first heating/annealing. Curve B—first cooling. Curve C—second heating/annealing. Curve D—second cooling. Curve E—final heating scan.

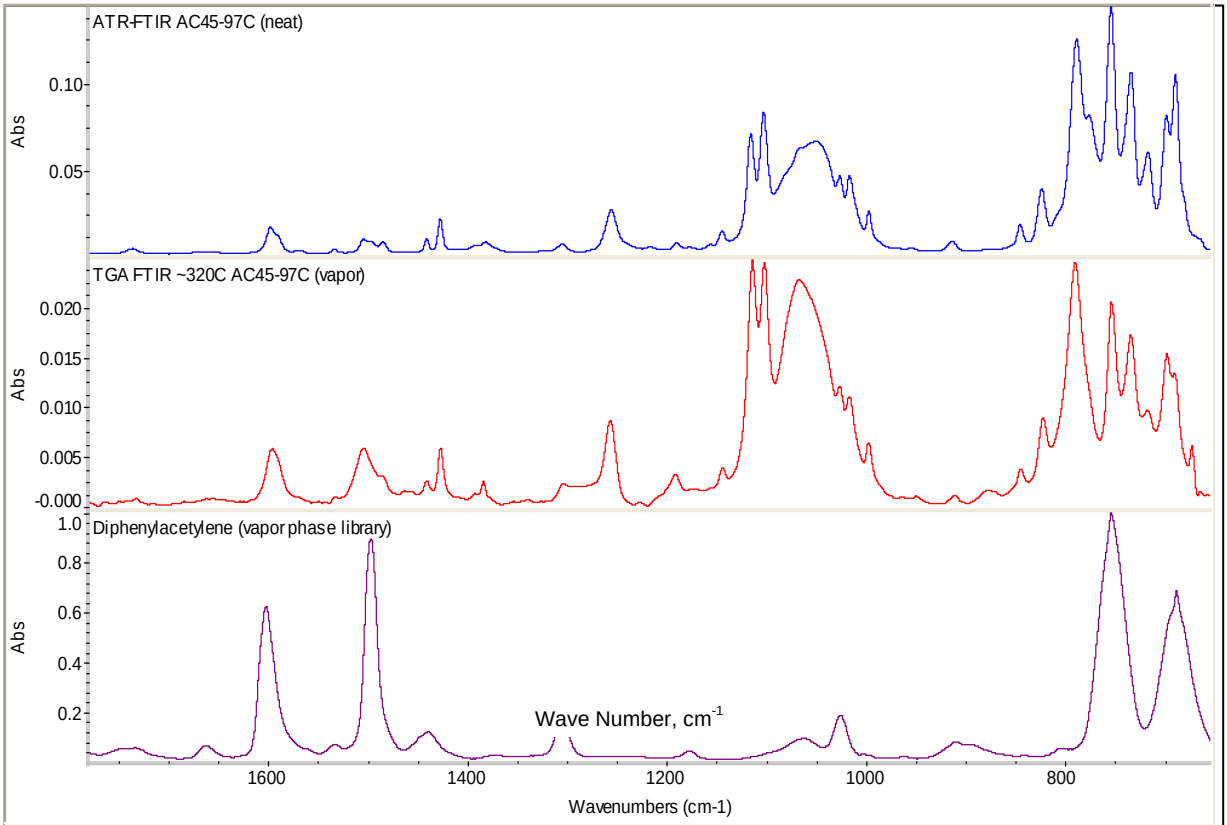
FIGURE 6. DSC Thermogram in Air of Vacuum-Dried Resin.

The cumulative time in the curing zone (above 290°C) was about an hour. It is possible that the Tg would have increased even more had the sample been cured for a longer time at 380 to 400°C. The Tg becomes nearly impossible to measure by DSC as crosslinking increases because the Tg broadens. In the future, the plan is to perform a dynamic mechanical analysis to estimate the Tg and modulus as a function of high-temperature curing.

TGA-FTIR SPECTRAL ANALYSIS

In the TGA-FTIR apparatus, a sample of 2PEPPSi2 was heated at 10°/min to 320°C (in nitrogen) and held there for 20 minutes. The initial release of ethyl acetate was observed. The FTIR spectrum of the TGA off-gas product(s) at 320°C was compared with the attenuated total reflectance FTIR spectrum of a neat film of liquid 2PEPPSi2 at room temperature and to a library spectrum of vapor-phase diphenylacetylene (Figure 7). The important finding is that the major product in the hot off-gas was the 2PEPPSi2 resin itself.

The ratio of PEP end groups to siloxane appears to be nearly unchanged when comparing the neat film with the off-gas. Note that the 2PEPPSi2 resin is 58% by weight PEP end groups; therefore, it would be difficult to detect a small amount of unattached diphenylacetylene (tolane). In the off-gas, the PEP end groups of the resin retain the characteristic peaks of tolane and thus would not appear to be converted to other compounds lacking the acetylene functional group.

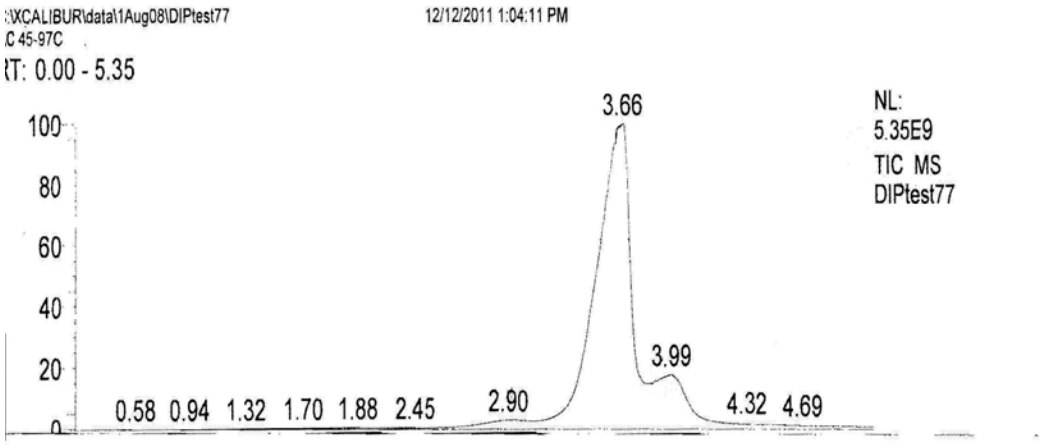


Note: Top (**blue**), a film of neat 2PEPPSi2 at ambient temperature; middle (**red**), TGA off-gas from 2PEPPSi2 at 320°C; bottom (**purple**), a vapor-phase library spectrum of diphenylacetylene. (Abs = absolute, ATR = attenuated total reflectance.)

FIGURE 7. FTIR Spectra From 4,000 to 650 cm^{-1}.

DIP-MS ON 2PEPPSI2

Liquid resin was placed in a quartz micro tube and inserted into the MS chamber (~20 mTorr) using a direct insertion probe. During analysis, the probe was maintained at 30°C for 30 seconds, then heated to 450°C at 100°C/min, and held at 450°C for 5 minutes. The relative abundance of molecular masses (total ion current) as a function of time came in three distinct clusters, as shown in Figure 8.



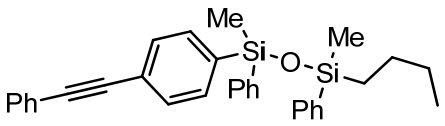
Note: The mass of ions appeared in three clusters centered at 2.9, 3.7, and 4.0 minutes.

FIGURE 8. Relative Abundance of Total Ion Current as Function of Time (Minutes) Indicated by Smooth Curve.

The very large (second) cluster of ions (maximum at 3.7 minutes) was largely the ion with a mass of 610 daltons (this is the mass of 2PEPPSi2). In this same large cluster, lesser amounts of two other ions were observed: the one in larger abundance was 417 daltons, and the one in smaller abundance was 517 daltons. Reasonable fragments of PEPPSi2 can be suggested for those masses.

The third ion cluster (maximum at 4.0 minutes) was much smaller in relative abundance. It contained compounds resulting from trisiloxane and tetrasiloxane impurities in the as-received monomer from Gelest, as mentioned earlier. Those impurities resulted in the corresponding PEP-terminated molecules. The molecular weight of these molecules was one at 747 daltons and the other at 882 daltons. The 747 ion was two times more abundant than the 882 ion. Five additional fragments were two times more abundant than the 747 ion: 209, 219, 258, 266, and 517. Four additional fragments had about the same abundance as the 747 ion: 178, 295, 339, and 417.

The first cluster of ions (maximum at 2.9 minutes) was a very small cluster. One ion had a mass of 490 daltons. This ion was possibly the monobutylated compound (Figure 9) resulting from excess n-butyllithium used in the lithiation procedure. The monobutylated compound probably made up less than 2% of the total resin, according to TGA. The fragment of this compound minus the butyl group was also found (433 daltons).



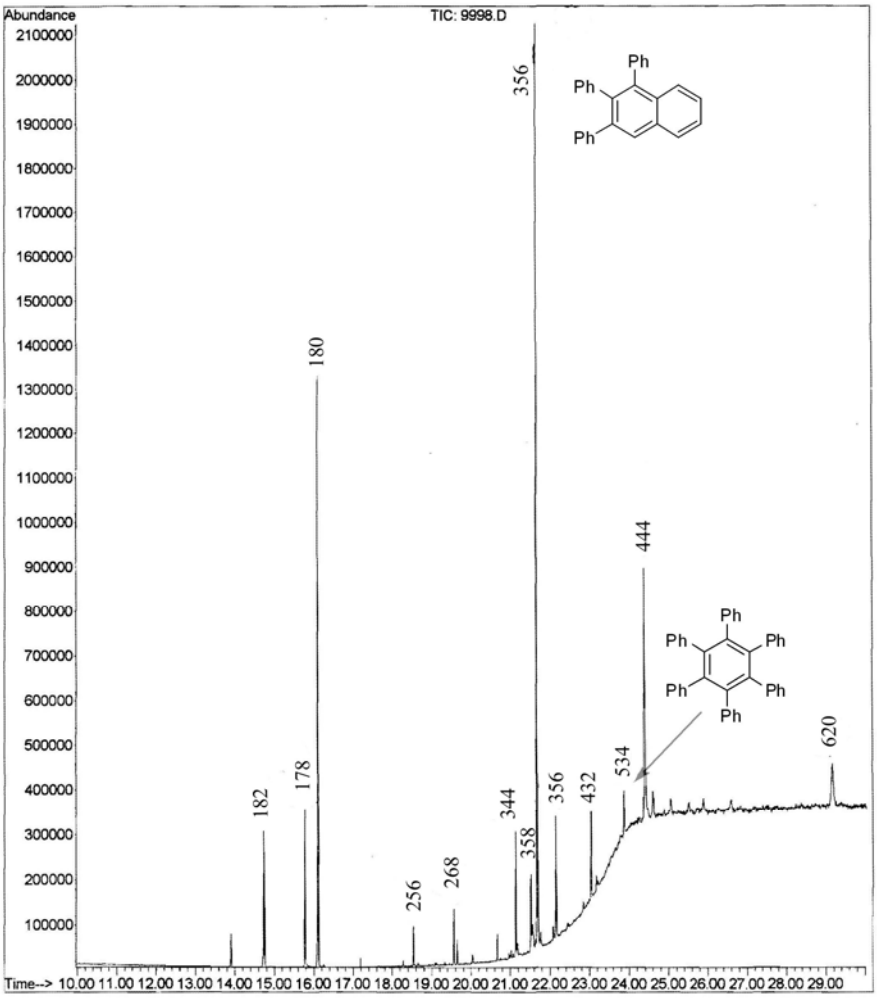
Note: Impurity resulting from use of excess n-butyllithium in synthesis of 2PEPPSi2

FIGURE 9. Small Amount of Impurity Found in DIP-MS Analysis.

Two ions in larger relative abundance in this very small cluster had masses of 178 and 355 daltons. The smaller one was likely tolane, and the large one, a dimer of tolane (see the next section on thermolysis of tolane). The fact that this first ion cluster was very small in abundance in contrast to the large second ion cluster and the fact that PEP makes up 58% of the mass of 2PEPPSi2 reinforce the conclusion that PEP end groups were not split off by thermolysis, even at 450°C (but more likely by DIP-MS ion impact).

THERMOLYSIS OF TOLANE: A MODEL REACTION FOR CROSSLINKING CHEMISTRY

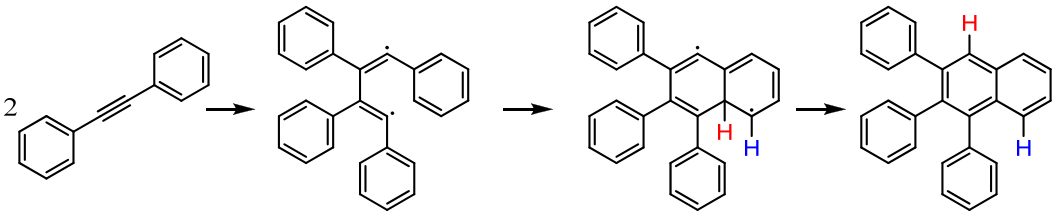
The thermolysis of tolane (diphenylacetylene) was used as a model reaction to help understand the curing mechanism of the 2PEPPSi2 resin. About 0.5 gram diphenylacetylene was sealed in a thick-walled 2-inch-long Carius tube and placed into a sand bath heated to 350°C for 90 minutes. There was likely a small amount of air in the tube. After the heat treatment, the tube was removed from the bath and broken open. A small amount of solid was dissolved in dichloromethane to make a ~100-ppm solution. Approximately 1 µL of this solution was injected into the GC/MS. The GC inlet temperature was 250°C. The column oven was held at 40°C for 3 minutes, then heated at 10°C/min to 350°C, and held at 350°C for 60 minutes. The resulting chromatogram is shown in Figure 10. The number above each peak is the molecular mass of the parent compound eluting from the GC column. Elution from the GC column was monitored for 60 minutes, but the last compound to elute was observed at approximately 29 minutes.



Note: The number above the peak is the molecular mass of the parent compound. Time is in minutes.

FIGURE 10. GC/MS Chromatogram of Products From Thermolysis of Tolane.

The most abundant species (retention time ~21.5 minutes) had a molecular mass of 356. It was hypothesized that this peak resulted from the dimerization of tolane to form the tetraphenyl butadiene diradical, which then rotated and cyclized to form the stable final product of triphenyl naphthalene (see Figure 11). Triphenylazulene (356 daltons) could be the small peak eluting at ~22.2 minutes.

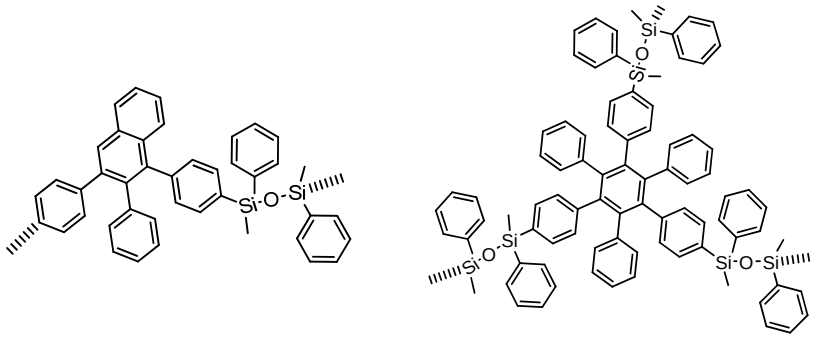


Note: The most abundant compound produced has a molecular mass of 356 daltons and is likely triphenyl naphthalene.

FIGURE 11. Most Abundant Compound Produced in Thermolysis of Tolane.

Stilbene (molecular mass 180) was the second-most abundant compound found in the thermolysis product mixture. A smaller amount of 1,2-diphenylethane (182) was found. Surprisingly, a compound of 444 molecular mass was the third-most abundant compound. The 444 and the 620 compounds contain 2.5 and 3.5 times the mass of the starting tolane in their respective structures (an indication of the incorporation of a benzyl-type radical). The fully aromatic hexaphenylbenzene (534) was observed, the expected trimer of tolane. The 432 compound is possibly tetraphenylnaphthylene (one carbon short of incorporating 2.5 tolane molecules).

These data indicate that the cure chemistry most likely generates a large fraction of chain-extending (linear-chain) junctions involving the triphenyl naphthalene structure, as well as a smaller fraction of chain-crosslinking junctions involving the hexaphenylbenzene structure. These all-aromatic structures should be extremely stable and should greatly increase the modulus of the cured material. Examples of the two types of junctions (with attached disiloxanes) suggested by these data are shown in Figure 12. Three additional isomers are possible for the naphthyl-containing chain-extending junction (left side), and two isomers are possible for the crosslinking junction (right side).



Note: A chain-extending all-aromatic junction (left) and a chain-crosslinking all-aromatic junction (right).

FIGURE 12. Suggested Structures That Form in Cured PEP-Terminated Resins.

CONCLUSIONS AND RECOMMENDATIONS

High-temperature curing of the PEP-terminated silaryl-disiloxane monomer affords a tough, hard matrix material stable to 450°C. Results from thermolysis of tolane, a model compound for PEP, indicated that cyclic dimerization and trimerization of PEP could be forming polyaromatic chain extensions and crosslinks, respectively, during thermal curing. This new monomer (2PEPPSi2) is superior to the analogous per-methyl and per-phenyl monomers in that it is less volatile than the former and more easily processed than the later. The per-methylated monomer is very volatile (50% mass loss by TGA) before reaching the onset of the curing temperature (320°C). The per-phenylated monomer is highly crystalline (210°C melting point). In so much as the monomer of this study is very slow to crystallize (T_m = 98°C) and has 11% mass loss (under the same conditions), this level is too much. To obviate the volatility problem, the curing temperature could be lowered using catalysts. Furthermore, it is highly recommended to explore increasing the molar mass of the monomers by changing the shape to that of a star shape, which is less likely to crystallize and should have a lower viscosity than a linear monomer of the same molar mass.

The siloxane unit is the key structure for maintaining the liquid state of these resins. The curing temperature of the PEP end groups (320 to 390°C) is high enough to afford a long pot life for the process of filling the fiber preform prior to cure. It is recommended that slight modifications to the PEP reactive groups be explored to lower the curing temperature to the 250 to 290°C range.

The synthetic approach of the present study gave a greater yield of product than the related literature-introduced methods. The bromotolane proved easy to prepare on a moderate scale (20 to 100 grams). This approach will also facilitate the synthesis of star-shape silarylene-disiloxanes (in progress).

These monomers should be useful in blends with other resins to achieve lower viscosity to improve resin flow during the fiber-infusion process and to make the composite more hydrophobic and thermally stable. This resin technology is very promising for developing an impact-resistant composite by blending larger star-shaped monomers with smaller linear monomers (and ceramic nanoparticles). On platforms traveling at hypersonic speeds, by the time the temperature reaches 1,100°F, this resin will have naturally formed a thermal-oxidative barrier coating. The high-temperature modulus and oxidation resistance of the cured part can be further enhanced by adding nano-silica (borosilicates, etc.) to the resin system.

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